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See Attached Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with None Proposed

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEETDate August 1, 1985Project No. A-4121~~EMSL~~/Lab EMSL

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Project Director(s) Joe N. HarrisGTRC / ~~EMSL~~Sponsor Sumitomo Cement Co., Ltd. Chiyoda-Ku, Tokyo, JapanTitle Ceramic to Metal Bonding Technology ReviewEffective Completion Date: 6/30/85 (Performance) 6/30/85 (Reports)

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- ☐ None
- ☒ Final Invoice or Final Fiscal Report
- ☐ Closing Documents
- ☐ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
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May 28, 1985

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Subject: Letter Reports Number 1 and 2, "Ceramic to Metal Bonding
Technology Review," for the periods April 1 - May 31, 1985,
Georgia Tech Research Institute Project A-4121

Gentlemen:

The months of April and May have been spent in manually searching the literature to cover the areas of ceramic to metal bonding specified in your 30 January TELEX and follow up letter of February 25, 1985. This manual search was conducted to establish categories to be examined in a computer literature search that is now being conducted. Telephone discussions have been held with colleagues from both U. S. Industry and U. S. Government. The information from these two sources is extremely limited due to proprietary and security reasons. Also industrial contacts are reluctant to provide cost information, except for finished products. Therefore, since we have received no input from Sumitomo on their costs, as requested in our proposal and since U. S. industry will not reveal this information our estimates of cost will have to be based on experience in our research laboratories. This will mean that our estimates may have large deviations from the actual costs for Sumitomo to fabricate ceramic metal joints in Japan.

During the month of June we will prepare our final letter report to you which will include a bibliography of relevant publications in the areas of interest to Sumitomo Cement Company including a concise Summary of the methods which should be considered. An experimental plan for testing and developing the most promising of the bonding systems identified will be provided.

Respectfully submitted,

 Joe N. Harris
Project Director

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A-4121

CERAMIC TO METAL BONDING
TECHNOLOGY REVIEW

By

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Georgia Institute of Technology
Georgia Tech Research Institute
Atlanta, Georgia 30332

June 1985

Prepared for

Sumitomo Cement Co. Ltd.
Central Research Laboratory
Chiba, Japan

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I. INTRODUCTION

The Sumitomo Cement Company, Ltd, requires an adhesive bonding system for ceramic (Al_2O_3 , Si_3N_4 , SiC) linings on metal (steel or stainless steel) machinery parts. The specific requirements for Sumitomo Cement's applications are: a tensile bond strength of 1000 kg/cm^2 (98.07 MPa) and a cost to manufacture of less than $180,000 \text{ Yen/m}^2$ ($\$750/\text{m}^2$). In previous investigations Sumitomo Cement did not find a system which met these two conditions.

The Georgia Tech Research Institute at the Georgia Institute of Technology has conducted a technology survey on ceramic-metal joining techniques by: (1) contacting U. S. Government Laboratories and U. S. Industrial Manufacturer's for state-of-the-art information, and (2) conducting an extensive literature survey using the facilities of the Price Gilbert Library at the Georgia Institute of Technology.

II. METHOD OF APPROACH

Sumitomo Cement requested that the results of the technology survey be broken down into types of bonding techniques as follows:

- A. Solid-Phase and Vapor-Phase Reaction Systems
- B. Solid and Liquid Reaction Systems
- C. Solid and Solid Reaction Systems
- D. Other Systems.

Contacts with colleagues in government and industry were made by telephone with follow-up submission of available literature. The open published literature was surveyed using both individual and computerized

search techniques. The published literature search was limited to the period 1965-1985.

III. RESULTS

The results of discussions with colleagues in industry and government produced very little information on processing and no information on costs. Information available from U. S. Department of Defense sources was not releasable to foreign nationals. A new development sponsored by the U. S. Department of Energy, the bonding of partially phase stabilized zirconia was discussed openly and the process is described later in this report. However, the laboratory size specimens prepared at the Department of Energy cannot be related to mass production costs and the Department of Energy could not tell us what their laboratory costs were.

We experienced no better results with industry. All companies contacted would discuss the type of process used only in broad terms and none of the companies contacted would provide information on the cost to produce their products. All companies considered their cost information to be proprietary. Approximately 170 publications were reviewed in the area of ceramic-metal bonding, but only a very few were directly related.

IV. DISCUSSION OF RESULTS

A. Consultation with Colleagues in Government and Industry

1. The U. S. Department of Energy

a. The Oak Ridge National Laboratory (ORNL) has developed a

brazing process for applying ceramic structural insulation to the pistons in uncooled diesel engines. The leading piston candidate is nodular cast iron (NCI) and the leading structural insulation is partially stabilized zirconia. However, in the ORNL experimental work they have brazed several commercial aluminas, an experimental alumina-silicon carbide and silicon carbide to NCI, ferritic stainless steel and Ti bars. Two processes have been investigated: (1) an indirect brazing process in which the ceramic is coated with an active metal prior to brazing with a commercial filler metal, and (2) direct brazing with specially formulated filler metals to wet and bond to both metals and ceramics.

In the indirect brazing process PSZ is jointed to NCI at 735° C in vacuum (5×10^{-5} mm Hg) and utilizes treatment of the ceramic surface by an active element followed by brazing with a ductile, low melting filler material. The cast iron is also treated to enable the filler material to braze to it. Typical room temperature shear strength was 120 MPa. Using a transition piece that has a coefficient of thermal expansion between those of the two materials room temperature shear strength was increased to 187 MPa.

In the direct brazing process using experimental filler materials with alumina pads on ferritic stainless steels, shear strengths of over 200 MPa were achieved. All of these demonstration joints were made with a 2.5 centimeter diameter. Production costs have not been estimated, and the compositions of the experimental filler materials were not given. A brief synopsis of this program is given in the Ceramic Technology News Letter, published by the Oak Ridge National Laboratory 1/.

b. The Sandia National Labs have developed a process to produce high strength glass-ceramic seals compatible with Inconel 718. The glass-ceramic contains silica, boron oxide, alumina, phosphorous pentoxide, and alkali metal oxides. The Inconel 718 is a precipitation-hardened, nickel-based alloy, much stronger than standard stainless steel. The process produces high strength corrosion resistant seals capable of operating to 700° C. The U. S. Department of Energy has been awarded U. S. Patent No. 4,414,282 for the process 2/.

2. Cummins Engine Company

The Cummins Engine Company is involved in similar programs to the Oak Ridge National Laboratory work to develop pistons for uncooled diesel engines. A paper presented by Yonushonis and Wolter at the American Ceramic Society, Ceramic-Metal Systems Meeting in Cocoa Beach, Florida, Jan 21-23, 1985 3/ described Cummin's process and testing of PSZ bonded to ductile iron. The Cummins process uses an active metal brazing system similar to ONRL with a Ti-Cu-Ag filler metal. The major problem with this system is that the braze melting temperature is high enough to change the desired microstructure of the iron. No shear or tensile strength values were given.

The Cummins personnel also briefly described their work using GTE-Wesgo Mo-Mn alloys and a proprietary braze from Advanced Technologies in New Jersey designated as "Introgene."

3. Battelle Laboratories, Columbus, Ohio

Battelle has bonded PSZ to iron by diffusion using a copper interlayer followed by hot pressing. No data were available on tensile or shear strength or on cost to process.

4. DHR, Incorporated

DHR is using microwaves to cause fusion between a ceramic (dielectric) and metals. When microwave energy is applied specifically to the joint area between two such materials fusion can occur. The use of microwave radiation offers two advantages over more conventional low frequency induction methods: (1) by confining the electric fields, necessary for heating, to a microwave resonant structure much higher fields can be achieved for less power input, and (2) the energy is focused more easily on the desired region of the material.

DHR provides no information on specific materials but indicates that it has laboratory research facilities to study this concept for joining ceramics and metals.

5. Other U. S. Companies Contacted

A list of other U. S. Companies involved in ceramic-metal joining who were contacted are shown in Appendix A. None of these companies would give details of their process, or the cost to manufacture. Some of the companies gave a general description as follows:

a. Alberox Corp. utilizes alumina ceramics and sapphire bonded to steels using Ni-Au-Cu-Ag-Sn followed by electroplating.

b. Ceradyne Inc. uses a Mo-Mn-W paste fired onto the ceramic followed by Au-Cu-Ni and electroplating. Ceramic materials are: alumina, beryllia and sapphire.

c. Ceramaseal Inc. bonds Kovar or stainless steel to 95 percent alumina using Ag-Cu eutectic melting at 780° C. Active metals are pure silver + Au-Ni alloy with a 950° C melting point.

d. Coors Porcelain Company uses a Mo-Mn or Tungsten base metallization followed by standard plating with Ni, Au, Ag or Cu.

These companies primarily deal with hermetic seals, electrical feed throughs and tube to tube insulators.

e. GTE Wesgo-manufactures a series of brazing alloys with liquidus temperatures ranging from 705 to 1240° C.

B. LITERATURE SEARCH

A combined manual and computer literature search was conducted on ceramic metal bonding for the twenty year period 1965-1985. The ceramic materials covered were aluminum oxide, silicon carbide and silicon nitride bonded to steel or stainless steel. Also, because of the immense interest in structural ceramics for heat engine applications and the large amount of research currently in progress partially stabilized zirconia (PSZ) bonded to steel or cast iron was also included. This combined survey resulted in approximately 170 articles, but only a few of these 170 show direct applicability to the bonding of the above ceramics to steel or stainless steel. The articles have been subdivided into the four classes requested by Sumitomo Cement Company, Ltd, and are shown as references. The remaining articles are included as a bibliography.

1. Solid Phase and Vapor Phase Reaction Systems

Several solid-vapor reaction systems have the potential for use in ceramic metal bonding. These are vacuum evaporation, reactive evaporation, sputtering, chemical vapor deposition, and ion implantation. Vacuum evaporation (sometimes referred to as physical vapor deposition)

is an established deposition technique in which the material to be deposited is heated in a vacuum until a sufficiently high vapor pressure is achieved to cause material to condense on a nearby substrate at a suitable deposition rate. Modern systems use high-vacuum electron beam technology, which allows high evaporation rates, freedom from contamination, good control, and high thermal efficiency. Reactive evaporation is a modification of electron beam evaporation in which a gas such as oxygen, nitrogen or a hydrocarbon is metered into a vacuum chamber, where it reacts with a vapor from a metallic evaporant to form a metal oxide, nitride, or carbide coating. Instead of depending on heat to vaporize the material, as in evaporation, sputtering involves bombarding the target with energetic ions. The ion source can be an ion gun or more typically positive ions from a plasma, which are attracted to the negatively charged target. The ions transfer their energy through collisions with atoms of the target, which form a secondary-atom collision cascade. When this cascade intercepts the surface of the target, material is ejected. The advantage of sputtering over other processes, such as CVD, is that the substrate can be at low temperatures, which allows deposition onto non-refractory substrates and minimizes reaction with the substrate. Lower substrate temperatures also minimize room-temperature stresses induced by thermal expansion mismatch between the coating and substrate. Chemical vapor deposition is deposition of a solid onto a heated substrate surface as a result of chemical reactions in the gas phase. Advantages of the chemical vapor deposition process are: (1) deposition rate is high, (2) coating is typically more isotropic, denser, more thermally stable, and more adherent because of

high deposition temperature, (3) it is applicable to most oxides, carbides, nitrides, and borides. The disadvantages are: (1) high deposition temperature prohibits use on some non-refractory substrates, (2) corrosive and explosive gases are used, and (3) some reactants are very expensive. A number of techniques can be classified under the heading of ion implantation. Some methods use ions from a gun or plasma in conjunction with evaporation, sputtering, or chemical vapor deposition and thus could just as easily be classified under these topics. Other techniques rely strictly on higher energy ion beams for implantation or for mixing a previously deposited thin coating into the near surface region of the substrate.

Only four journal or textbook articles were found which describe the use of solid phase and vapor phase reaction systems as part of the process of forming a ceramic-metal joint meeting Sumitomo's stated requirements. These papers are broken down by category as follows:

a. Electron Beam-Physical Vapor Deposition (EB-PVD). Boone and Fairbanks in a 1980 publication 4/ describe the use of a dual source EB-PVD system to deposit Al_2O_3 and ZrO_2 layers, 25 to 250 μm in thickness on unidentified metallic substrates. Presumably the substrates were super-alloys since the application was for gas turbine components. The paper was very preliminary and no property data were given on the coatings or on the strength of the bond between coating and substrate. A considerable portion of the paper was devoted to a description of the coating equipment.

b. Sputtering Technique. Two papers 5,6/ dealt with sputtering as a method of applying metallic interlayers of Mo-Mn or, an active metal such as titanium instead of the more traditional paste application methods prior to brazing with a filler metal. In each case the sputtering technique was used as a first step prior to the final preparation of the ceramic-metal joint by the brazing process.

c. General. In a 1976 ASM publication Bunshah 7/ has written a seventy page chapter on the processes of physical vapor deposition, evaporation, ion plating and sputtering. This chapter covers free standing shapes as well as coatings sustained by a chemical or metallurgical bond to the substrate. This is an excellent review article, but does not deal in depth with ceramic-metal joining.

2. Solid and Liquid Reaction Systems

a. Organic Adhesives. No references in any English language publications were found to organic bonding systems which will operate above 500° C. An English language abstract of a Japanese language publication 8/ mentions organic bonding agents. However, translation of this article was not possible with the funds available for this program. The English language abstract indicates that this is a review article and lists most of the systems mentioned in the Sumitomo Cement telex of 30 January 1985.

b. Inorganic Adhesive. The category of inorganic adhesive in solid-liquid phase systems is covered by a number of processing techniques which are described in the sub-categories below.

(1) Brazing. The Sumitomo Cement telex of 30 January 1985 uses the term soldering under the category "Solid and Liquid Reaction System. The U. S. Literature prefers the term "brazing." Kohl 9/ states "The difference between soldering and brazing is primarily marked by the temperature level at which either is performed and to which the joint can be exposed later in service before it fails." In either soldering or brazing the parent metal and ceramic or metallized ceramic surface are heated to less than the melting point of either component. The joint is then achieved by the addition of a metal alloy, either the solder or the braze filler metal. However, there is a difference in the mechanism by which the bond is established. In soldering adhesion comes about by alloying and diffusion in a thin surface film, and a substantial quantity of the bulk solder is left in the joint. In brazing, alloying and diffusion consume most of the filler metal. Therefore, the primary difference besides temperature comes down to the gap width between the metal and the metallized ceramic. Since Sumitomo Cement has placed a specification of 500° C operating temperature no "soldered" systems for joining refractory ceramics to steel or stainless steel were found.

There are two general methods of brazing ceramics to metals: the molybdenum-manganese method which has been known since 1936 10,11/ and the active metal filler metal method which seems to be in more general use today.

In the moly-manganese process 12/ a mixture of molybdenum (80 percent) and manganese (20 percent) powder is suspended in a nitrocellulose binder and applied to the ceramic surface by one of several techniques to produce a layer of up to 50 μ m thickness. After drying the

coated ceramic is fired in a wet hydrogen (dew point 25°C) atmosphere at temperatures of 1300 to 1550°C depending on the type of ceramic. The fired layer is 25-30 μm thick and the ceramic is ready to be brazed to a metal body if filler metals are used which wet the molybdenum layer.

For brazing to steel or stainless steel using a silver-copper eutectic mixture it is first necessary to nickel plate the molybdenum layer and in turn sinter in a dry reducing gas. The above process works for alumina ceramics containing up to 97 percent Al_2O_3 . For higher alumina content ceramic material it is necessary to add a reactive component in the form of an active metal or hydride of that metal.

The active metal process has been in use since 1947 13/. It involves the application of high melting point oxygen active metals: titanium, zirconium, tantalum, or niobium to a ceramic surface. This is followed by brazing to a metal part with a brazing filler metal. The active metal can be applied as a metal hydride or by the use of an active metal incorporated in the brazing alloy. This operation requires close temperature control and must be carried out in a vacuum of at least 1.33×10^{-3} mPa or in a pure neutral gas such as argon.

A third process known since 1961 and designated by Klomp 12,14/ as the frit process is a one step process wherein a thin layer of molten metal oxides form a seal between ceramic parts or metal-to-ceramic parts. The oxide mixtures are composed of components in the system $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ or $\text{Al}_2\text{O}_3\text{-MnO-SiO}_2$. Mixtures of the first system mentioned can be used for sealing refractory metals to ceramics at 1200°C or higher. The second system listed above is used for sealing iron alloys to ceramics at 1140°C . These seals can operate up to 800°C .

Some more recent applications in sealing the ceramics of interest: Al_2O_3 , SiC and Si_3N_4 by brazing methods are as follows.

The most recent publication surveyed (February 1985) by Iseki, et al., 15/ describes the brazing of silicon carbide to 316 stainless steel. Iseki joined both reaction bonded silicon carbide (RB-SiC) and pressureless sintered (PLS-SiC) silicon carbide using various filler metal alloys composed of silver, copper and titanium. The reaction bonded silicon carbide containing ten weight percent free silicon required a much higher weight percent titanium in the filler metal alloy to promote wetting of the ceramic-steel joint at 950°C . The silver-copper-titanium alloy can serve two purposes: (1) it melts at a temperature low enough to preserve the steel grain structure, and (2) it provides a ductile zone to reduce strains between the ceramic and metal which have vastly different thermal expansions. However, in the case of the RB-SiC and stainless steel joint the free silicon diffuses into the copper-silver alloy, forming intermetallic compounds and makes the filler metal brittle.

For satisfactory wetting of the joint area the reaction bonded silicon carbide required an alloy filler metal of 59 wt percent Ag-23 wt percent Cu -18 wt percent Ti. The pressureless sintered silicon carbide was bonded to the stainless steel using an alloy consisting of 70.9 wt percent Ag -27.6 wt percent Cu and 1.5 wt percent Ti. Brazing conditions were 950°C for two hours in vacuum ($6 \times 10^{-3}\text{ Pa}$). Tensile strength values were not reported but shear strengths of 65 MPa at temperatures below 400°C were reported for the PLS-SiC and 45 MPa for the RB-SiC bonds to stainless steel. A transition material in the brazement might have increased shear strengths.

Another Japanese author, Okamoto 16,17/ joined low carbon steel and stainless steel to alumina ceramics using copper filler metal in a slightly oxidizing atmosphere. The author attributes the strong bond between alumina and steel to the formation of Hercynite (FeAl_2O_4).

A somewhat similar process was described by Burgess, Neugebauer and Flanagan 18,19/ in 1975 for joining of copper metal to alumina, beryllia, silica and various spinels. It is also stated that the process described has been used to bond copper to various metals. The paper does not indicate however that the copper was used as an intermediate layer to bond ceramics to other metals. But a 1976 patent 20/ indicates the process can be used to bond alumina to iron. The process described uses a copper foil placed on the ceramic and a partial pressure of oxygen to form a copper oxygen eutectic with a melting point of 1065°C . This is 18°C below the melting point of copper, hence one can have a melted skin of copper-oxygen eutectic while maintaining the structural integrity of the unmelted copper film. The copper-oxygen eutectic skin is then the adhesive to bond to the ceramic. Strengths in excess of 138 MPa were reported for bonds between the copper and oxygen containing ceramics.

Another reference to brazing of alumina or other ceramics to steel is found in the Russian literature. Kruchinin and Metelkin 21/ describe a study whereby improving the ceramic surface finish also improved bond strength between metal and ceramic. Bond strength was also dependent on brazing temperature when using an active metal brazing process. Bending force values between iron and alumina as high as 284 MPa were reported for a brazing temperature of 1070°C . Many other references are found for brazing of alumina to other metals but not specifically to steel or

stainless steel. These references are included as part of the bibliography.

(2) Sprayed Coatings. Flame and plasma sprayed coatings of aluminum oxide and other ceramics on metal substrates were investigated extensively in the United States in the late 1950's and early 1960's. Most of the articles on spray coating of ceramics on metal were published prior to 1965 and consequently were not picked up by the computerized literature survey.

The Engineering Experiment Station (EES) of the Georgia Institute of Technology conducted considerable research in the area of applying ceramic coatings on steel by flame spray and arc plasma techniques. A series of summary (annual) reports for the period 1957-1961 describe these efforts 22/. No property data are given for bond strength but a tensile strength of 33 MPa was obtained for the aluminum oxide coating with metal substrate removed.

Another EES report describing arc plasma coating parameters for aluminum oxide on Type 304 stainless steel was published in 1968 23/. This work was primarily for rain erosion protection and the only mechanical property data given is for resistance to impact. All of the EES reports describe attempts to overcome stresses created by the difference in thermal expansion between aluminum oxide and stainless steel by using graded layers between the steel and aluminum oxide. The only post 1965 U. S. publication picked up by the computer survey 24/ describes an intermediate metal fiber pad brazed to the parent metal on one side and coated with a ceramic by plasma spray on the other. The

fiber metal pad acts as a strain absorbing compliant interlayer to take up the stress caused by the difference in expansivity between ceramic and metal substrate. Coatings 1.5 to 3 millimeters in thickness were retained intact on metal substrates through conditions of severe thermal shock. The major problem with this technique was the very low tensile strength of the metal fiber pad in the Z direction (2 MPa).

The computer survey listed three articles in the Russian literature related to plasma spray coatings on metal. The first, a 1969 article by Lyashenko et al. 25/, describes a pin and disk technique for measuring the adhesion strength of aluminum oxide coatings on steel. The parameters for plasma spraying of aluminum oxide on steel of Grade St3 is not described, however, values for the adhesion strength are given. The maximum strength of 9.3 MPa was achieved with a coating thickness of 0.6 mm. At thicknesses greater than 0.7 mm adhesion failures occurred. There was no speculation as to the mechanism of adhesion failure. A 1970 Russian article by Zakharov and Trofimov 26/ describes spray conditions for both zirconium oxide and aluminum oxide onto a steel substrate. Arc plasma spraying conditions were compared with gas flame spraying conditions using a rod type gas flame gun. In all cases a graded undercoat was used with a thickness of approximately 0.1 mm and with a total thickness of either zirconia or alumina of 0.4 to 0.5 mm. Both uncooled and cooled substrates were used. The uncooled substrate spraying distance was 70 mm and the cooled substrate spraying distance was 45 mm. Adhesion strengths as high as 16.5 MPa were reported. The third Russian article by Bytin and Shirokov 27/ describes the spraying of copper and an active metal: titanium, zirconium, or tin. The ceramic

substrates are identified with code letters and numbers so the type of ceramic is not known. Adhesion values range from 1.7 to 3.4 MPa for the copper substrate only. The copper-titanium film to ceramic substrate had adhesive strengths of 2.1 to 4.8 MPa. The copper tin films had adhesive strengths to the ceramics of 2.8 to 4.0 MPa.

3. Solid and Solid Reaction Systems

Klomp 28,29/ has prepared two review articles on solid state bonding of ceramics to metals. In these review articles Klomp describes the functions of pressure, temperature and time as the parameters of the solid state bonding of metals to oxide materials. Klomp states "the function of pressure in the solid state bonding of the oxygen active metals to oxide materials is to create a highly active metal surface by the in situ destruction of the surface oxide layer. The flowing metal must also be expected to affect the contamination on the surface of the oxide material." He further states "the function of temperature is to activate the interaction by increasing the mobility of the atomic species and also the mobility of the dislocations in the metal. The latter is found with a decrease of the flow stress of a metal and with an increase of the creep rate with increasing temperature." He states "the bonding time, i.e., the time the pressure is maintained will have a great effect if a chemical reaction occurs between the materials. If such reactions do not occur, the time required to deform the metal is the determining parameter, and so the deformation rate should be as high as possible to prevent oxygen penetration at the interface during the bonding process."

The Sumitomo Telex of January 30, 1985 gave several terms under the category solid and solid reaction systems. High pressure bonding and

diffusion-reaction bonding were separated. The articles found under the category solid and solid reaction system cannot be separated in this matter. High pressure bonding includes diffusion and therefore the following category (a) covers both.

(a) High Pressure-High Temperature Bonding. Suganuma, et al., 30/ in a 1983 publication described a new method for solid state bonding between ceramics and metals. To bond iron and alumina he used a composite interlayer composed of 60 volume percent Fe and 40 volume percent Al_2O_3 . The conditions were 1573 K and 2.1 GPa for 30 minutes. After bonding the interlayer was composed of homogeneously distributed iron and alumina. The author gives no mechanical strength figures but postulates that the system will produce bonded materials with high strength and good thermal shock resistance. In a later paper Suganuma 31/ describes the bonding of aluminum oxide to steel using the interlayer method and hot isostatic pressing at 1273 to 1575 K under 100 MPa for 30 minutes using a laminated interlayer of niobium/molybdenum. The main bonding strength of 3 samples using the niobium/molybdenum laminated layer was 63 MPa. Calow 32/ describes the solid state bonding of $\alpha\text{-Al}_2\text{O}_3$ single crystal plates to nickel, chromium and nichrome sheets. Ni- Al_2O_3 bonding couples were prepared at 1100° C under a pressure of 13.8 MPa for 2 hours. The average bond strength varied from 4.9 to 49 MPa depending on die material. The die materials were graphite, graphite-alumina, stellite-alumina. Bond strength increased as reducing conditions decreased, that is, the stellite-alumina die inserts gave the best bond strengths. Chromium- Al_2O_3 bonding couples were produced under a vacuum of 1.33 Pa. Bonding was conducted at a temperature of 1000 to

1300° C with pressures of 7.7 to 45 MPa and pressing times of 1/2 to 7 hours. The bonding was found satisfactory at 1100° C with a bonding strength of 70 MPa. The higher bonding strength for the chrome alumina couples was attributed to the solubility of chrome oxide and aluminum oxide. Nickel/chromium-Al₂O₃ bonds were prepared in two ways. The first was to alternate layers of nickel and chromium sheet. The second was to use a commercial nichrome material containing a small percentage of silicon. Using alternate layers of nickel and chromium between the aluminum oxide, specimens were prepared at 1100, 1200 and 1300° C for pressing times varying between 1/4 and 5 hours. One has to assume that bonding pressure was between 7.7 and 45 MPa since the pressures are not given in the article. Bonds made with the chrome strip in contact with the alumina were stronger than those made with the nickel strip in contact with alumina. With the chromium in contact with alumina strengths of 70 MPa were achieved. For the commercial nichrome material strengths of 70 to 84 MPa were achieved, but pressing pressures greater than 30 MPa causes a reduction in bondi silicon content of the commercial nichr

Metelkin, Makarkin and Pavlova 33/ technique. This technique is also refer or diffusion method and is covered by US February 1961. A 99.5 percent aluminum under the following conditions: a pressi of 1300° C and a time of 10 minutes. Str For welding under a vacuum of 0.013 Pa a achieved. When welding in hydrogen with

present the bending strength was 108 to 127 MPa. In both cases failure was by tears in the ceramic. When welding alumina to stainless steel it was found necessary to add silica to the alumina or deposit silicon metal on the surface of the stainless steel.

(b) Solid State Brazing. One article was found on the solid state brazing of silicon nitride. In this paper Becher and Halen 34/ described the brazing of silicon nitride to silicon nitride using zirconia as a filler material. The brazing of the two hot pressed pieces of silicon nitride which were 0.63 cm thick and had diamond ground mating surfaces took place by placing -325 mesh cubic zirconia in an alcohol slurry on one of the silicon nitride mating surfaces. The two silicon nitride pieces were then pressed together to form a silicon nitride/zirconia/silicon nitride sandwich. The samples were brazed by holding at temperatures of 1350 to 1500° C for one hour and either a vacuum of 0.013 Pa or an argon atmosphere while applying a small compressive load of 1.4 MPa to maintain the alignment of the sandwich sample. The zirconia braze layer was typically 0.25 mm in thickness. The brazed pieces were tested in 3 point bending with fracture occurring in the zirconia layer at stresses of 155 to 225 MPa rather than by catastrophic failure. No articles were found on brazing silicon nitride to steel or stainless steel, however, this paper suggests that the zirconia brazed layer could be used to braze the silicon nitride to these materials.

Elssner, Diem, and Wallace 35/ described similar work to that of Becher in 1980 except that they also added niobium to the zirconium innerlayer between the silicon nitride layers. Specimens were bonded at

1150° C for 2 hours using 14 MPa mechanical loading. Two thicknesses of niobium foil were used 0.35 mm and 1 mm thickness. Specimens made with the 0.35 mm thick niobium foil fractured in the foil area. Specimens made with the 1 mm thick foil failed within the ceramic. The thicker niobium layer apparently relieved the stresses due to the differences in thermal expansion between the zirconia and silicon nitride.

4. Other Methods

Articles by Borbidge 36,37/ describe a system called solid-state reaction bonding for joining metals to ceramics. This process has primarily been used for bonding two pieces of ceramic with a metal, usually gold or platinum, but it is stated that transition metals, that is iron, cobalt, nickel and copper, can be bonded to ceramics such as alumina, zirconia, magnesia, silica and beryllia. The solid state reaction bonding procedures are simple and have the following characteristics: (1) the bonding temperature lies below the melting point of the lowest melting component in the system which is generally the metal and it is usually about 90 percent of the melting point of the metal in degrees Kelvin. (2) Usually an air atmosphere can be used, but argon or vacuum can be used if necessary. (3) Only light clamping pressures are used just enough to insure good physical contact at the interface during bonding (0.5-0.15 MPa). (4) The bonding times varies from a few seconds to about 3 hours. (5) The ceramic to be bonded must be polished to a finish approaching optical flatness to achieve maximum bond strength.

No other alternate methods of any consequence were found. Therefore, the remaining articles are attached as a bibliography for further reading in Appendix B.

V. BONDING SYSTEMS

There are two general bonding systems which will meet the requirements of Sumitomo Cement, Ltd. These are brazing and solid state diffusion. There are several modifications to brazing systems, all of which exceed the 100 MPa tensile bonding strength requirement. These brazing systems use an active filler metal or the older process described by Klomp 12,14/ wherein mixtures of $\text{Al}_2\text{O}_3\text{-MnO-SiO}_2$ are used for sealing iron alloys to ceramics at 1140°C . The active metal process requires the use of an active metal such as titanium or zirconium. The active metal can be applied by a vapor deposition process directly to the ceramic and then the braze metal used to bond the ceramic to the stainless steel or steel substrate. A second method is to incorporate the active metal directly into the brazed alloy and then bond the ceramic and metal with this material. This bonding process is usually done in vacuum or in a neutral atmosphere and requires no special tooling except a furnace which will maintain the vacuum or the neutral atmosphere. The solid-state pressure bonding or, as it is sometimes referred to, reaction welding requires special dies for each piece to be welded. However, the close temperature requirements and vacuum or neutral atmosphere requirements are not necessary in this process. No recommendation can be made at this time as to which process best meets Sumitomo Cement, Ltd., requirements.

Absolutely no information was obtained on cost for this process. Sumitomo Cement did not provide us with any of their figures and no information could be obtained from government laboratories or from private industry in the United States. The government laboratories did

not work on production quantities and industry considered this information to be proprietary and would not release these figures.

VI. RECOMMENDATIONS

Since both the brazing process and the solid state diffusion process hold promise to meet the requirements of Sumitomo Cement any number of systems could be recommended in an experimental plan for testing and developing joints. The Georgia Tech Research Institute has all of the equipment necessary to look at vapor deposition of active metals on ceramics, to form brazed joints with active metal, with moly-manganese or with the $\text{Al}_2\text{O}_3\text{-MnO}_2\text{-SiO}_2$ type of fillers. We also have or could construct easily the necessary equipment to accomplish solid state diffusion. We suggest that the active metal brazing process be examined in our laboratory whereby the active metal would be applied to a high purity alumina ceramic by vapor deposition or by incorporating it into the brazed filler metal. These two methods would be examined in parallel and tensile strength values measured on the specimens obtained. A record of cost would be kept so that the cost per square meter could be calculated based on our laboratory cost. Also solid-state diffusion methods could be examined in our laboratory and the same information obtained on the specimens prepared. We recommend that Sumitomi Cement consider this approach and if appropriate, GTRI would be pleased to prepare a proposal to cover a detailed research plan and to establish costs for manufacture of such ceramic metal joints.

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APPENDIX A

U. S. Companies contacted for information on Ceramic-Metal Bonding.

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Industrial Park,
New Bedford, MA
617/995-1725
2. Bridgeport Specialty Metals
1875 McCarter Highway
Newark, N. J. 07104
201/481-3100
3. Ceradyne, Inc.
3030A S. Red Hill Avenue
Santa Ana, CA 92705
714/549-0421
4. Ceramaseal Division,
Clevopak Corp.
Box 25
New Lebanon Center, N. Y. 12126
518/794-7800
5. Coors Porcelain Company
600 Ninth St.
Golden, CO 80401
303/278-4000
6. Detoronics
10660 E. Rush St.
S. El Monte, CA 91733
818/579-7130
7. Engineered Materials Div.
Hi-Purity Materials Inc.
Box 363
Church Street Station
New York, N. Y. 10008
212/662-8200
8. GTE Products Corporation
477 Harbor Blvd.
Belmont, CA 94002
414/592-9440
9. Latronics Corporation
1001 Lloyd Avenue
P. O. Box 469
Latrobe, PA 15650
412/539-1626

10. Varian Associates
EIMAC Division
301 Industrial Way
San Carlos, CA 94070
415/594-4001

APPENDIX B

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a. Vapor Deposition

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